

III.B.4 Design and Development of New Carbon-Based Sorbent Systems for an Effective Containment of Hydrogen

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Objectives

- Develop carbon-based solid-phase and liquid-phase hydrogen storage materials with capacities of >6 wt. % and >45 g H₂/L.
 - Discover novel substrates using experimental and computational methods.
 - Optimize selected materials and catalysts and demonstrate cycling stability.
- Develop hydrogen storage system prototype with 6 wt. % and 45 g H₂/L capacity at temperature in the range of -40 to 90-120°C and H₂ pressure of less than 1000 psia.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- B. Weight and Volume
- C. Efficiency
- G. Life Cycle and Efficiency Analyses
- Q. Regeneration Processes for Irreversible Systems
- R. By-Product Removal

Approach

- Liquid-phase materials (“liquid hydrides”) that store hydrogen by reversible hydrogenation and are regenerated by efficient processes offboard vehicles, utilizing the existing liquid fuels infrastructure for transportation.
- Solid materials that store hydrogen by temperature/pressure reversible hydrogenation or by physical adsorption, thus enabling regeneration onboard vehicles.

Accomplishments

- Discovered liquid hydrides that store >5.5 wt. % H₂ and >50 g H₂/L and operate at temperatures <200°C.
- Initial cycling experiments show no chemical degradation of the liquid hydrides or systematic hydrogenation/dehydrogenation rate changes over 5-7 cycles.

- Using high-level predictive models, identified >10 potential solid/liquid substrates with dehydrogenation temperatures (temperatures for 95% dehydrogenation at equilibrium with 1 atm H₂ and dehydrogenated substrate) of <150°C.

Future Directions

- Continue integrated experimental and computational discovery effort to identify new liquid/solid substrates with suitable hydrogen capacity and operating temperature.
- Conduct catalyst screening and catalyst development to increase rates of hydrogenation and dehydrogenation.
- Initiate a study to investigate cycling stability and substrate/catalyst lifetime.
- Computationally screen conceptualized novel ionic solids in terms of hydrogen capacity and heat of adsorption. Synthesize promising candidate ionic solids for experimental determination of hydrogen capacity and heat of adsorption.

Introduction

An efficient, cost-effective hydrogen storage system is the key enabling technology for the widespread introduction of hydrogen fuel cells to the domestic marketplace. Although the development of PEM (proton exchange membrane) devices is maturing to small-scale, low-volume commercialization, major impediments still exist for the use of fuel cells for personal transportation and other portable applications, in which hydrogen supply and production are at a mismatch. Effective, safe hydrogen storage is required to resolve this issue. Hydrogen storage becomes particularly important due to the inability to effectively use fossil fuels as the primary energy source for producing the hydrogen fuel onboard vehicles. The market requires energy storage capacities, size, and weight of packages that will safely store the hydrogen fuel and be suitably integrated with the fuel cell power device. None of the existing technologies for hydrogen storage (compressed and liquid hydrogen, metal hydrides) meet all or even most of the necessary criteria such as safety, low cost, and high volumetric and gravimetric density. New technologies are needed to realize the benefits of hydrogen as a clean, renewable energy carrier.

Approach

Air Products researchers are developing liquid-phase hydrogen storage materials ("liquid hydrides") that can be reversibly hydrogenated, allowing the storage of hydrogen in a safe, easily transportable

form. The liquid hydrides can be hydrogenated at large central or regional sites in locations where inexpensive hydrogen is available. Hydrogenation in an industrial facility allows for maximum overall energy efficiency through recovery and use of the heat generated by the exothermic hydrogenation. The hydrogenated liquid hydride could be distributed, using the existing liquid fuels infrastructure, to distribution sites where the liquid would be dispensed to hydrogen-powered vehicles. Onboard a vehicle powered by a hydrogen fuel cell (FC) or hydrogen internal combustion engine (ICE), the liquid would pass through heat exchanger(s) and catalyst to release hydrogen and deposit the "spent" carrier into a separate tank. The amount of waste heat available from either a FC or ICE is sufficient to supply the necessary energy for the endothermic dehydrogenation reaction. Assuming a reasonable gravimetric hydrogen capacity (6 wt. %) and density (1 g/cc), 4 kilograms of hydrogen would be contained in only 18 gallons of a liquid hydride.

Another potential hydrogen storage system under investigation consists of a pressure/temperature, H₂-reversible, solid sorbent material that is packaged in a lightweight container under a modest pressure of hydrogen. The proposed sorbents that we have been investigating are novel, carbon-based compositions that can take up and contain hydrogen by either a reversible chemical mechanism in which the gas is stored in the form of carbon-hydrogen bonds, or by a strongly interactive physical process in which the H₂ molecule remains intact. We are exploring both such "chemical" (liquid) and "physical" (solid) sorbent

types, since each may provide materials that are optimal for different applications. Our reasoning is that the hydrogen is more "tightly" held in the chemical sorbents and therefore operates at low equilibrium pressures with potential benefits in safety and use of packaging. Physical sorbents, in which the H₂ molecule is retained as such, while perhaps requiring more "forcing" conditions (i.e., higher H₂ pressures), may be expected to have lower heats and faster H₂ sorption and desorption kinetics.

Results

Liquid-Phase Carriers

In our discovery efforts to date, we have identified a number of promising liquid-phase hydrogen carriers. One specific composition (LQ*H₂) has a gravimetric and volumetric hydrogen capacity range that easily meets the 2005 DOE targets and may also reach the 2010 DOE targets. Low-temperature dehydrogenation is facilitated by the low heat of hydrogenation for this substrate (-12.1 kcal/mol H₂). This material property compares favorably with previously touted liquid-phase hydrogen carriers such as *trans*-decalin (heat of hydrogenation = -15.8 kcal/mol H₂), which is more difficult to dehydrogenate. The liquid hydride composition also has a very low vapor pressure, ca. 10 torr at 200°C, which allows for an easy separation of the product hydrogen from the dehydrogenated liquid without a need for condensers or membranes.

Our liquid-phase hydrogen carrier (LQ*H₂) can be dehydrogenated to provide hydrogen and the dehydrogenated carrier (LQ*) at a temperature lower than any known liquid-phase hydrogen carrier. Under 1 atm hydrogen pressure, the LQ*H₂ can be heated with catalyst to 197°C to evolve hydrogen gas. The LQ* can be re-hydrogenated in the same reactor, and the process operated in a cyclic mode. After 5 cycles, the liquid carrier retained the ability to store over 5.5 wt. % hydrogen, and there was no systematic change in the rate of dehydrogenation (Figure 1). The low volatility of both LQ*H₂ and LQ* allowed for the measurement of multiple cycles in the same reactor, with no perceptible loss of liquid due to evaporation.

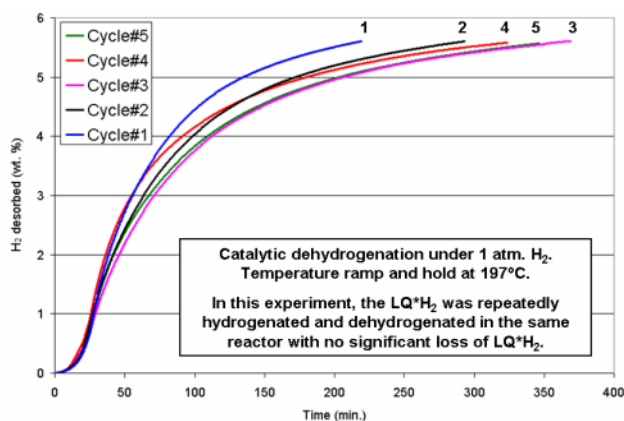


Figure 1. Cycling of the LQ* + H₂ ↔ LQ*H₂ System with Hydrogenation at 140°C and <1000 psia H₂ and Dehydrogenation at 197°C and 15 psia H₂

As part of our discovery effort in this first year of DOE funding, we have identified by high-level computational means a number of individual compositions that are predicted to have a low heat (enthalpy) of hydrogenation (Figure 2). A low heat of hydrogenation results in a desirable low theoretical dehydrogenation temperature at equilibrium. We have calculated the temperature at which, at equilibrium, a 95% conversion of LQ*H₂ to dehydrogenated LQ* will take place under 1 atm of hydrogen. This calculation has allowed us to show that our identified compositions have a much lower dehydrogenation temperature than the previously used hydrogen carriers cyclohexane and *cis*-/*trans*-decalin. A number of compositions have been identified in our computational discovery effort that have a 95% dehydrogenation temperature <120°C.

Solid-Phase Carriers

We have identified a number of solid-state, carbon-based compositions that will reversibly store hydrogen also by a reversible chemical hydrogenation/dehydrogenation process under pressure/temperature swing conditions in the presence of suitable catalysts. One composition has shown the ability to absorb over 3.5 wt. % hydrogen at 150°C under 1000 psia hydrogen. This solid hydrogen storage composition will release the hydrogen in a pressure/temperature swing mode,

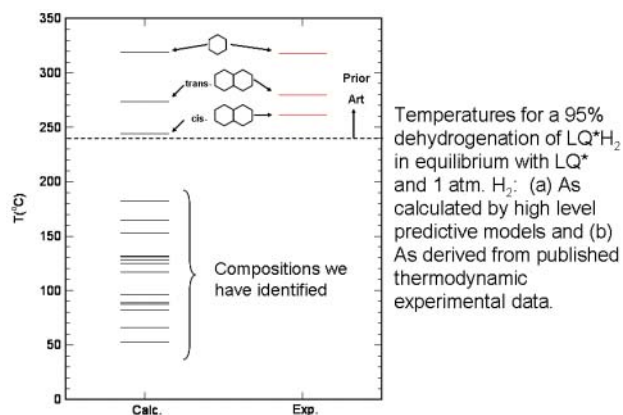


Figure 2. Calculated Temperatures for a 95% Dehydrogenation of LQ*H₂ Composition at 1 atm H₂ (The prior art systems are *cis*- and *trans*-decalin/naphthalene and cyclohexane/benzene.)

with a decrease in hydrogen pressure to 18 psia and an increase in temperature to 180°C (Figure 3). However, our present solid-state hydrogen storage compositions have rates of hydrogen uptake and release that are far slower than the liquid hydride compositions.

Ionic Solid Carriers

The possibility of storing hydrogen by physical adsorption on novel carbon-based ionic solids has been explored through high-level predictive calculations. Hydrogen adsorption on porous ionic solids was simulated with periodic density functional theory under the generalized gradient approximation. We first performed full energy minimization on the coordinates of the atoms in the selected unit cell and the cell parameters. This allowed us to obtain the H₂ adsorption structure and energetics at 0 K. The calculated adsorption energies at 0 K for our model ionic solid are -7.98 kcal/mol H₂ for one H₂ molecule per unit cell, -4.97 kcal/mol H₂ for two H₂ molecules per unit cell, and -4.95 kcal/mol H₂ for three H₂ molecules per unit cell, suggesting that the adsorption energy decreases as the H₂ loading increases. For adsorption at a finite temperature, we performed molecular dynamics simulations (constant particle number, volume, and total energy) using density functional theory in the canonic ensemble for 5 picoseconds with the step size of 1 femtosecond. At ambient temperature, the calculated adsorption

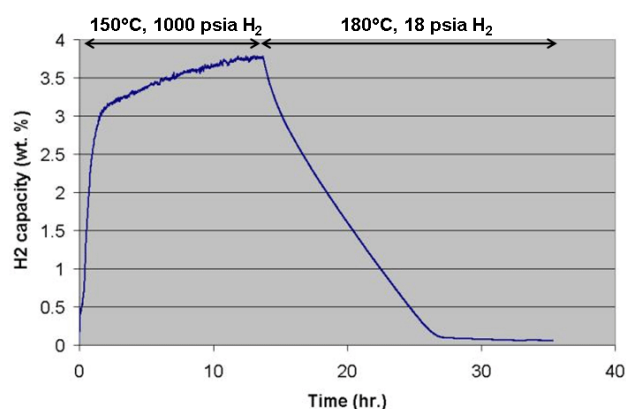


Figure 3. Hydrogen Uptake by a Carbon-Based Solid Admixed with a Catalyst, Showing an H₂ Uptake at 150°C and 1000 psia H₂ and Hydrogen Release at 180°C and 18 psia H₂

energy becomes -1.41 kcal/mol H₂ for one H₂, -0.31 kcal/mol H₂ for two H₂, and -0.94 kcal/mol H₂ for three H₂ molecules per unit cell, respectively. To enhance the adsorption energy, we are currently performing *ab initio* molecular dynamic simulations on ionic solids that have a higher ionic charge density.

Conclusions

- A liquid-phase hydrogen carrier has been identified which provides a >5.5 wt. % H₂ and >50 g H₂/L capacity operating in a temperature/pressure swing mode. The carrier provides a flow of H₂ at *ca.* 1 atm at <200°C, much milder conditions than reported for liquid carriers of the prior art. Our liquid-phase hydrogen carriers can be regenerated (most likely offboard vehicles) by a direct catalytic reaction with hydrogen.
- Solid-state, carbon-based compositions have been identified which also function as temperature/pressure hydrogen carriers in the presence of suitable catalysts. However, their hydrogenation/dehydrogenation rates are slower than the above liquid system.
- Novel, carbon-based, ionic solid compositions have been identified that, by quantum mechanics/molecular dynamics calculations, show an interaction energy with molecular hydrogen, a property that could render them useful as hydrogen carriers. However, the H₂

interaction energies of the first systems we have studied have to be enhanced if the solids are to have useful hydrogen storage capacities at ambient temperature.

FY 2004 Publications/Presentations

1. FreedomCAR Hydrogen Storage Tech. Team Review (2/19/04): "Design and Development of New Carbon-based Sorbent Systems for an Effective Containment of Hydrogen" by Alan C. Cooper and Guido P. Pez.
2. DOE Hydrogen Program Technical Review (5/25/04): "Hydrogen Storage by the Reversible Hydrogenation of Liquid and Solid Substrates" by Alan C. Cooper and Guido P. Pez.